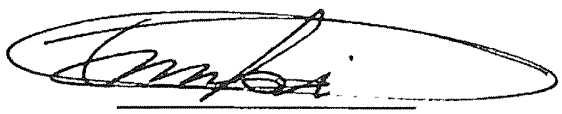
STATEMENT OF ACCURACY

I, Toshifumi Onuki, c/o TMI ASSOCIATES of 23rd Floor, Roppongi Hills Mori Tower, 6-10-1, Roppongi, Minato-ku, Tokyo 106-6123, Japan, do solemnly and sincerely declare that I well understand the Japanese and English languages and that the attached English version is full, true and faithful translation made by me this 22nd day of October 2009 of the granted claims of the Japanese Patent Application No. 2004-380885 filed before the Japanese Patent Office on the 28th day of December 2004.

In testimony whereof, I have hereunto set my name and seal this 22nd day of October 2009.

October 22, 2009



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[Claim 1]

A magenta ink composition, wherein when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is -38 or more to -29 or less.

[Claim 2]

The magenta ink composition according to claim 1, wherein the L* value in accordance with the CIE standard is 60 or less.

[Claim 3]

A magenta ink composition, wherein the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 5 or more in a diluted aqueous solution with a pigment concentration of 2×10^{-3} g/L.

[Claim 4]

The magenta ink composition according to any one of claims 1 through 3, comprising at least C. I. Pigment Violet 32 and Pigment Violet 19 as the pigment.

[Claim 5]

The magenta ink composition according to claim 4, wherein the mixing ratio of the C. I. Pigment Violet 32 and the C. I. Pigment Violet 19 is 1 : 2 to 2 : 1.

[Claim 6]

The magenta ink composition according to claim 4 or 5, wherein the sum concentration of the C. I. Pigment Violet 32 and the C. I. Pigment Violet 19 is 4 wt.% or less.

[Claim 7]

The magenta ink composition according to any one of claims 1 through 6,

comprising a 14-30 wt.% organic solvent with a high boiling point.

[Claim 8]

The magenta ink composition according to claim 7, wherein the organic solvent with a high boiling point includes glycerin.

[Claim 9]

The magenta ink composition according to any one of claims 1 through 8, comprising a pigment as a coloring material and also a dispersant for dispersing the pigment at 10-140 wt.% based on the pigment.

[Claim 10]

The magenta ink composition according to any one of claims 1 through 9, comprising a 1-20 wt.% permeation enhancer.

[Claim 11]

The magenta ink composition according to any one of claims 1 through 10, comprising 0.01-5 wt.% of at least one of acetylene glycol-type compound and silicone-type compound.

[Claim 12]

An ink cartridge comprising the magenta ink composition according to any one of claims 1 through 11.

[Claim 13]

A recording method for forming an image by using the magenta ink composition according to any one of claims 1 through 11.

[Claim 14]

A recording system for forming an image by using the magenta ink composition according to any one of claims 1 through 11.

[Claim 15]

A recorded matter where an image is formed by using the magenta ink composition according to any one of claims 1 through 11.

[Name of Document] Specification

[Title of the Invention] MAGENTA INK COMPOSITION, INK CARTRIDGE, AND RECORDING METHOD, RECORDING SYSTEM AND RECORDED MATTER USING THE MAGENTA INK COMPOSITION

[Technical Field]

[0001] The present invention relates to a novel magenta ink composition, and more particularly to a magenta ink composition that demonstrates excellent color reproducibility in a high-chroma and low-lightness region, excellent granularity and increased luster, and suppresses clogging of ink-jet ejection heads.

[Background Art]

[0002] An ink using a pigment such as C. I. Pigment Red 202 or C. I. Pigment Red 122 has been suggested as a magenta ink for color ink jet recording (for example, Patent Document 1).

[0003] When C. I. Pigment Red 202 and C. I. Pigment Red 122 are used, sufficient color reproducibility in a high-chroma and low-lightness region cannot be obtained unless the concentration of pigments in the ink is comparatively high. However, if the pigment concentration increases, the ink viscosity tends to increase and responsiveness of meniscus tends to become high. For this reason problems are easily associated with the printing speed, quality, and head life. Furthermore, if the pigment concentration is increased, a smooth ink film is difficult to form on a lustrous media and luster of the recorded matter is sometimes degraded.

[0004] A method of decreasing the quantity of glycerin added to the ink is employed to prevent the ink viscosity from increasing.

[Patent Document 1]

Japanese Patent Application Laid-open No. 2003-268275

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0005] However, because glycerin functions as a wetting agent preventing clogging in ink-jet ejection devices, the ink can easily cause clogging if the content of glycerin is decreased. Furthermore, the conventional magenta inks excel in color reproduction of dark sections with an L* value of the recorded matter of 40 or less, but granularity is insufficient.

[0006] Hence, the object of the invention is to provide a magenta ink that excels in color reproducibility in a high-chroma and low-lightness region and excels in granularity, and suppresses clogging of ink-jet recording heads, and has increased luster.

[Means for Solving the Problem]

[0007] The results of the comprehensive study conducted by the inventors demonstrated that a magenta ink comprising C. I. Pigment Violet 32 and C. I. Pigment Violet 19 as coloring materials has excellent color reproducibility in a high-chroma and low-lightness region even at a comparatively low pigment concentration.

[0008] According to another aspect of the invention based on this finding, provided is a magenta ink composition, wherein when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is -38 or more to -29 or less. It is further preferable that the L* value in accordance with the CIE standard of this magenta ink composition be 60 or less.

[0009] Furthermore, the present invention also provides a magenta ink composition in which the a* value in accordance with the CIE standard that is calculated from a

visible absorption spectrum be 5 or more, preferably 7 or more, in a diluted aqueous solution with a pigment concentration of 2×10^{-3} g/L.

[0010] All the above-described magenta ink compositions demonstrate excellent color reproducibility in a high-chroma and low-lightness region despite a comparatively low concentration of coloring material. Therefore, the increase in the ink viscosity caused by increased concentration of coloring material can be prevented. In addition, the magenta ink compositions also excel in a granularity of printed matter. The granularity as referred to herein is a characteristic making it possible to suppress granular appearance caused by dot representation during image formation.

[0011] Furthermore, because of the above-described features of the magenta ink composition in accordance with the invention, a wetting agent such as a high-boiling organic solvent with a high viscosity can be added in a sufficient amount. Therefore, even when printing is conducted by using an ink-jet method, the recording head is prevented from clogging.

[0012] According to another aspect of the invention, provided is a recording method for forming images by using the magenta ink composition. With this recording method, good recorded images with increased luster and excellent granularity and color reproducibility in a high-chroma and low-lightness red region can be obtained.

[0013] According to another aspect of the invention, provided is a recording system for forming images by using the magenta ink composition. With this recording system, good recorded images with increased luster and excellent color reproducibility in a high-chroma and low-lightness red region can be obtained.

[0014] According to another aspect of the invention, provided is a recorded matter where images have been formed by using the magenta ink composition. This recorded matter is of high quality, excels in color reproducibility in a high-chroma and

low-lightness red region and also has excellent granularity and increased luster.

[Best Mode for Carrying Out the Invention]

[0015] [Magenta Ink Composition]

The magenta ink composition in accordance with the invention will be described below based on preferred embodiments thereof.

[0016] In the magenta ink composition in accordance with the invention, as described hereinabove, an magenta ink composition is contained in which when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is -38 or more to -29 or less, preferably the b* value is -38 or more to -33 or less. Such magenta ink excels in color reproducibility in a ultraviolet region, the sRGB color space, which is brightness system coloring, can be color reproduced in a wide range on a recording medium, and the ink can be advantageously used for Desktop Publishing (DTP). On the other hand, if the b* value becomes less than -38, the coloring ability of red color deteriorates.

[0017] Furthermore, in the magenta ink composition in accordance with the invention, in addition to the condition relating to b* value, it is preferred that the L* value be 60 or less when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum in a diluted aqueous solution with a dilution ratio of 10,000 or less is 80. With such a structure, color reproduction in a high-chroma and low-lightness region is possible.

[0018] The L* value, a* value, and b* value in accordance with the CIE standard that are calculated from the visible absorption spectrum can be obtained by transmittance measurements carried out by using, e.g., a device U3300 manufactured by Hitachi Ltd. at a scan speed of 600 nm/min, measurement wavelength range 380-800 nm, and slit

width 2.0 nm and conducting calculations at a view angle of 2° with a D65 light source.

[0019] Furthermore, the magenta ink composition in accordance with the invention preferably has the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum of 5 or more, preferably 7 or more, in a diluted aqueous solution with a pigment concentration of 2×10^{-3} g/L. In particular, from the standpoint of color reproducibility of a high-chroma region, the a* value is preferably 8 or more, more preferably 9 or more. The a* value can be also obtained by a method similar to the above-described measurement method.

[0020] The magenta ink composition in accordance with the invention preferably comprises C. I. Pigment Violet 32 (hereinafter abbreviated as "PV32") and C. I. Pigment Violet 19 (hereinafter abbreviated as "PV19") as pigments. In this case, the magenta ink composition in accordance with the invention can provide sufficient color reproducibility at a comparatively low concentration of PV32 and PV19 with respect to a high-chroma and low-lightness region. The total concentration of the PV32 and PV19 is 4 wt.% or less, preferably 2 wt.% or less to prevent the viscosity of the ink from being too high.

[0021] In order to provide for excellent color reproducibility of a high-chroma and low-lightness red region and to obtain excellent granularity, it is preferred that the mixing ratio of C. I. Pigment Violet 32 and C. I. Pigment Violet 19 be 1 : 2 to 2 : 1.

[0022] As discussed above, the magenta ink of the present invention preferably contains both PV32 and PV19, but the type of pigment is not particularly limited as long as the b* value is at least –38 but no more than –29 (and preferably the L* value is also 60 or less) given an a* value of 80 according to the CIE standard as calculated from the visual absorption spectrum in a 10000 x or lower dilute aqueous solution, or

else the a* value is 5 or more according to the CIE standard as calculated from the visual absorption spectrum in a dilute aqueous solution with a pigment concentration of 2×10^{-3} g/l. The magenta ink of the present invention needs to contain neither PV32 nor PV19, or may contain PV32 or PV19. For example, C. I. Pigments Red (hereinafter abbreviated as "PR") 5, 7, 12, 48 (Ca), 48 (Mn), 57 (Ca), 57:1, 112, 122, 123, 168, 184, 202, 207, 209 can be contained individually or in combinations of two or more thereof. Those pigments may be also combined with PV32 and/or PV19.

[0023] The magenta ink in accordance with the invention preferably comprises an organic solvent with a high boiling point in an amount of 14-30 wt.% as a wetting agent. Because the magenta ink in accordance with the invention makes it possible to obtain the target color reproducibility even at a comparatively low pigment concentration, a sufficient amount of organic solvent with a high boiling point can be added without increasing the viscosity. When an organic solvent with a high boiling point is added in the case of applications for ink jet recording, the ink is prevented from drying and clogging of the ink-jet printer head is inhibited. Examples of organic solvents with a high boiling point include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexane triol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane, alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether, organic alkalis such as urea, 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, and triethanolamine, and saccharides such as sugar alcohol. Those solvents are used

individually or in combinations of two or more thereof.

[0024] In particular, in order to prevent clogging and increase luster of the recorded image, it is preferred than the magenta ink composition in accordance with the invention has glycerin added thereto at a ratio of 14 wt.% or more. An organic alkali such as triethanolamine may be added together with glycerin. Triethanolamine also can function as a pH adjusting agent and dispersion stabilizer for the ink and is preferably used within a range of 0.1 to 10 wt.% in the ink.

[0025] The magenta ink composition in accordance with the invention preferably uses a pigment as a coloring material and comprises a dispersant for dispersing the pigment. Any dispersant that can be used with the pigment ink of this type can be employed without any limitation. Examples of suitable dispersants include cationic, anionic, and nonionic polymer dispersants of surfactants. Examples of anionic polymer dispersants include polyacrylic acid, polymethacrylic acid, acrylic acid – acrylonitrile copolymer, vinyl acetate – acrylic acid ester copolymer, acrylic acid – acrylic acid alkyl ester copolymer, styrene – acrylic acid copolymer, styrene – methacrylic acid copolymer, styrene – acrylic acid – acrylic acid alkyl ester copolymer, styrene – methacrylic acid – acrylic acid alkyl ester copolymer, styrene – α-methylstyrene – acrylic acid copolymer, styrene – α-methylstyrene – acrylic acid – acrylic acid alkyl ester copolymer, styrene – maleic acid copolymer, vinyl naphthalene – malefic acid copolymer, vinyl acetate – ethylene copolymer, vinyl acetate – fatty acid vinyl ethylene copolymer, vinyl acetate – maleic acid ester copolymer, vinyl acetate – crotonic acid copolymer, and vinyl acetate – acrylic acid copolymer. Furthermore, examples of anionic surfactants include sodium dodecylbenzene sulfonate, sodium laurate, and ammonium salts of polyoxyethylene alkyl ether sulfate, and examples of nonionic surfactants include polyoxyethylene alkyl ether, polyoxyethylene alkyl ester,

polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkylamine, and polyoxyethylene alkylamide. Those dispersants can be used individually or in combinations of two or more thereof. From the standpoint of dispersion stability of the pigment, styrene (meth)acrylic acid copolymers are preferred.

[0026] The dispersant is preferably contained at 10-140 wt.%, more preferably 10-100 wt.%, and even more preferably 10-60 wt.%, calculated as solids, based on the weight of the pigment. The content ratio of the dispersant in the ink is preferably 0.1-10 wt.%, more preferably 0.3-3 wt.%, calculated as solids.

[0027] Furthermore, from the standpoint of increasing the ability to wet a recording medium and permeation ability of ink, the magenta ink composition in accordance with the invention preferably contains a permeation enhancer. Examples of permeation enhancers include alcohols such as methanol, ethanol, and iso-propyl alcohol, lower alkyl ethers of polyhydric alcohols such as ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, propylene glycol monobutyl ether, and dipropylene glycol monobutyl ether, and diols such as 1,2-pentanediol and 1,2-hexanediol. Those enhancers can be used individually or in combinations of two or more thereof. It is preferred that diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, or 1,2-hexanediol, or combinations of two or more thereof be used.

[0028] The permeation enhancer is contained preferably at a ratio of 1-20 wt.%, more preferably 1-10 wt.% in the ink.

[0029] Furthermore in order to increase the ability of the magenta ink composition in accordance with the invention to wet a recording medium and permeation ability of ink similarly to the permeation enhancer, various surfactants such as anionic surfactants,

nonionic surfactants, cationic surfactants, and amphoteric surfactants can be used. It is especially preferred that acetylene glycol compound or silicon compounds be used. Commercially available compounds can be used as the acetylene glycol compounds. Examples of such compounds include Olfine Y and Surfynol 82, 440, 465, 485 (all are the trade names, manufactured by Air Products and Chemicals Co., Ltd.), Olfine STG, Olfine E1010 (both are trade names, manufactured by Nisshin Chemical Co., Ltd). Those compounds can be used individually or in combinations of two or more thereof. It is especially preferred that Olfine E1010 and Surfynol 465 be used. Furthermore, polysiloxane compounds such as BYK347, 348 or BYKUV3510 (manufactured by BYK Chemie Japan Co., Ltd.), which are commercial products, can be used as silicone compounds. The content ratio of the acetylene glycol compound and/or silicone compound is preferably 0.01-5 wt.%, more preferably 0.1-1.0 wt.%, and even more preferably 0.1-0.5 wt.%.

[0030] In order to shorten the drying time of ink, the magenta ink composition in accordance with the invention can comprise an organic solvent with a low boiling point. Examples of organic solvents with a low boiling point include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, sec-butanol, tert-butanol, iso-butanol, and n-pentanol. Those solvents can be used individually or in combinations of two or more thereof. Monohydric alcohols are especially preferred.

[0031] The magenta ink composition in accordance with the invention comprises the above-described components, such as pigment, dispersant, organic solvent with a high boiling point, permeation enhancer, acetylene glycol compound, and/or silicon compound and usually contains water as the balance. Pure water or ultrapure water such as ion exchange water, reverse osmosis water, ultra-filtrated water, and distilled water is preferred as the water. In particular, water obtained by sterilizing the

above-mentioned water by ultraviolet radiation or addition of hydrogen peroxide is especially preferred because it prevents the appearance of mold or bacteria over a long period.

[0032] If necessary, the magenta ink composition in accordance with the invention can additionally comprise additives such as a fixing agent such as water-soluble rosin, an antiseptic and a bactericidal agent such as sodium benzoate, an antioxidant and a UV absorber such as allophanates, a chelating agent, an oxygen absorber, and a pH adjusting agent. Those additives may be used individually or in combinations of two or more thereof.

[0033] The magenta ink composition in accordance with the invention can be prepared in the same manner as the conventional pigment inks by using the conventional well-known equipment, for example, a ball mill, a sand mill, an attritor, a basket mill, or a roll mill. In the preparation process, coarse particles can be removed by using a membrane filter or a mesh filter.

[0034] No specific limitation is placed on the application of the magenta ink composition in accordance with the invention, but it is preferably used in an ink-jet recording method, which is a recording method in which fine droplets of an ink are ejected from a nozzle and the droplets are caused to adhere to a recording medium to form the images of letters or figures. It is especially preferred that the magenta ink composition in accordance with the invention be used for on-demand ink-jet recording. Examples of on-demand ink-jet recording methods include a piezoelectric element recording method by which recording is conducted by using piezoelectric elements disposed in a printer head and a thermal heat recording method by which recording is conducted by using thermal energy, e.g., of a heater with a heat-generating resistance element disposed in a printer head. The magenta ink composition in accordance

with the invention can be advantageously used in any such ink-jet recording method.

[0035] The magenta ink composition in accordance with the invention can be employed, without limitations, with recording media that are usually used for ink-jet recording methods as a recording media for forming images, and it is preferably employed with the media having a coating layer or the usual paper (recording media in which fibers are exposed on the recording surface). In particular, if the magenta ink composition in accordance with the invention is employed on a media having a coating layer, then a significant suppression of granular appearance caused by dot representation during image formation can be obtained.

[0036] In the present specification, "media having a coating layer" means all the media where the surface (recording surface) where an image is formed by using the above-described magenta ink composition is covered at least with a coating layer. The media having a coating layer usually has a luster at 85° of 120 or less. Here, the luster at 85° is measured with "PG1M" manufactured by Nippon Denshoku Kogyo K. K. For the measurements, the measurement device is adjusted in advance so as to obtain a 85° luster of a standard luster plate of 100.

[0037] Mirror-finish media with a 85° luster of 70-120, for example, media having a resin coat layer where the contour of an image of a fluorescent lamp can be visually confirmed when the media is illuminated with the fluorescent lamp from a distance of 1 m or more can be used as such media having a coating layer. "PGPP (Premium Glossy Photo Paper) manufactured by Seiko-Epson Co., Ltd. Which has a 85° luster of 81 is a representative example of such media.

[0038] Other examples of media having a coating layer include semigloss media with a 85° luster of 10-70 and a matted media with a 85° luster of 10 or less.

[Recording Method]

The recording method in accordance with the invention will be described below.

[0039] The present invention is a recording method for forming images by using the abovementioned magenta ink composition, that is, a method for forming images by using a magenta ink composition in which when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is –38 or more to -29 or less (more preferably the L*value is 60 or less), or a magenta ink composition in which the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 5 or more in a diluted aqueous solution with a pigment concentration of 2×10^{-3} g/L). The recording method employing the abovementioned magenta ink composition is especially preferred. The recording method in accordance with the invention is implemented similarly to the usual recording method for ink jet recording, except that it uses the above-described magenta ink composition.

[0040] The recording method in accordance with the invention makes it possible to obtain images with increased color reproducibility in a high-chroma and low-lightness red region and also improved granularity and luster.

[0041] In the recording method in accordance with the invention, the image is preferably formed so that the ink weight at Duty 100% is 7-13 mg/inch^2.

[0042] Furthermore, in the mixed color, an image is preferably formed so that the ink weight at Duty 120% is 8-16 mg/inch^2.

[0043] In the present specification, "Duty" is represented by the unit of D value defined and calculated by the following formula.

[0044] D = [(number of actually printed dots)/(longitudinal resolution $\times$ lateral resolution)] $\times$ 100. The Duty 100% means the maximum weight of ink of one color

for one pixel.

[Recording System]

The invention relates to a recording system for forming images by using the above-described magenta ink composition, and a recording system, e.g., a recording device such as an ink-jet printer, that uses the magenta ink compositions of the above-described embodiments is especially preferred.

[Recorded Matter]

The invention relates to a recorded matter where images are formed by using the above-described magenta ink compositions, and a recorded matter where images are formed by using the magenta ink compositions of the above-described embodiments is especially preferred.

[Modification Examples]

The invention advantageously provides the above-described embodiments, but it is not limited to those embodiments and can be changed in a variety of ways, without departing from the essence thereof.

[0045] The invention will be described below in greater detail with reference to the working examples of the invention and test examples, but the invention is not limited by those working examples.

[Preparation of Inks]

Magenta ink compositions (M1) and (M2) comprising pigment PV32 and PV19 were prepared as the magenta ink compositions in accordance with the invention.

[Working Example 1]

[0046]

<Working Example 1 (M1)>

C. I. Pigment Violet 32 2.0 wt.%

C. I. Pigment Violet 19 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[Working Example 2]

[0047]

<Working Example 2 (M2)>

C. I. Pigment Violet 32 1.0 wt.%

C. I. Pigment Violet 19 1.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 1.0 wt.%

Glycerin 20.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

Furthermore, a magenta ink composition (m1) for which C. I Pigment Red 202 (hereinafter sometimes referred to as "PR20") is used in place of PV32 and PV19, was prepared.

[0048]

<Comparative Example 1 (m1)>

C. I. Pigment Red 202 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.8 wt.%

Glycerin 12.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0049]

The results obtained in measuring the reverse-flow viscosity are shown in Table 1.

[0050] [Table 1]

	M1	M2	m1
Reverse-flow viscosity	3.6	3.6	3.6

[0051]

From these results, it appears that although magenta inks M1 and M2 have high glycerin concentrations of 14.0 wt% and 20.0 wt%, respectively, their viscosities are equivalent to that of m1, in which only 12.0 wt% of glycerin is added. This is probably due to the fact that the pigment concentration is relatively low in M1 and M2.

[0052] (Evaluation of Resistance to Clogging)

Resistance to clogging was evaluated for the magenta inks M1 and M2 comprising PV32 and PV19 (working examples 1 and 2) and magenta ink m1 containing PR202 (comparative example).

[0053] Ink cartridges filled with respective inks were prepared, and heads were filled

with the inks by using the ink cartridges in the entire row of unused ink-jet printers PX-G900 (manufactured by Seiko Epson Co.). Then, nozzle check was conducted by using a printer driver to verify whether an abnormality has occurred.

[0054] The ink cartridges were then removed, the heads were removed from the printers, and the heads were allowed to stay for 10 days in a thermostat at 40°C and a moisture content of 20%. After 10 days, the head and ink cartridges were mounted on the printers and nozzle check was carried out by using the printer driver.

[0055] When an abnormality has occurred, cleaning was conducted by using the printer driver, and nozzle check was then carried out again. When the abnormality was still detected, cleaning and nozzle check were repeated till the results of the nozzle check indicated a normal state.

[0056] As a result, the heads in which the entire row was filled with the magenta inks M1 or M2 showed a normal output of nozzle check after no more than five cycles of cleaning. On the other hand, the head in which the entire row was filled with the magenta ink m1 did not show a normal output of nozzle check even after five cycles of cleaning. Those results suggested that the magenta inks M1 or M2 have higher resistance to clogging of the head that the magenta ink m1 of the conventional example and are suitable for an ink jet method. This is apparently because M1 and M2 could contain glycerin, which serves as a wetting agent, at a high concentration due to a comparatively low pigment concentration.

[0057] (Measurement of L* value, a* value, and b* value of magenta ink in the case of variable Duty)

Inks comprising 4 wt.% PV32 + PV19 (mixing ratios 1 : 1, 2 : 1, and 1 : 2), an ink comprising 2 wt.% PV32 + PV19 (mixing ratios 1 : 1), an ink comprising 4 wt.% PR202, and inks each comprising 4 wt.% one of PV32 and PV19 were prepared as

magenta inks. The ink compositions are presented below.

[0058] <PV32 + PV19 (1 : 1) = total 4 wt.% (Working Example 1)>

C. I. Pigment Violet 32 2.0 wt.%

C. I. Pigment Violet 19 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0059] <PV32 + PV19 (1 : 1) = total 2 wt.% (Working Example 2)>

C. I. Pigment Violet 32 1.0 wt.%

C. I. Pigment Violet 19 1.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 1.0 wt.%

Glycerin 20.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0060] <PV32 + PV19 (2 : 1) = total 4 wt.% (Working Example 3)>

C. I. Pigment Violet 32 2.7 wt.%

C. I. Pigment Violet 19 1.3 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0061] <PV32 + PV19 (1 : 2) = total 4 wt.% (Working Example 4)>

C. I. Pigment Violet 32 1.3 wt.%

C. I. Pigment Violet 19 2.7 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0062] <PR202: 4 wt.% (Comparative Example 1)>

C. I. Pigment Violet 202 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.8 wt.%

Glycerin 12.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0063] <PV19: 4 wt.% (Comparative Example 2)>

C. I. Pigment Violet 19 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0064] <PV32: 4 wt.% (Comparative Example 3)>

C. I. Pigment Violet 32 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.8 wt.%

Glycerin 12.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

[0065] Those inks were printed on a medium having a coating layer, and L* value, a* value, and b* value in accordance with the CIE were measured. C* was then found by the following formula by using those values. C* value was found from $C^* = (a^{*2} + b^{*2})^{1/2}$, and h was found from $h = \tan^{-1}(b^*/a^*)$.

[0066] More specifically, each magenta ink was loaded into an ink-jet printer PM900C (manufactured by Seiko-Epson Co., Ltd.) and printing was conducted on the aforementioned PGPP (manufactured by Seiko-Epson Co., Ltd.) as an example of

medium having a coating layer and printed products were obtained. In the printing, each magenta ink was ejected by changing Duty from 15% to 255% (ink weight 10-11 mg/inch^2).

[0067] The L* value, a* value, b* value, C* value, and h value in accordance with the CIE were obtained by measuring at a view filed 2° with D50 light source by using device Macbeth SPM50 manufactured by Gretag Co.

[0068] The measurement results are shown in Tables 2 to 8.

[0069] [Table 2]

Working Example 1 <PV32 + PV19 (1 : 1) = total 4 wt.%>

Duty	L*	a*	b*	C*	h
255	33.41	72.57	12.91	73.71	10.09
130	34.23	73.99	8.52	74.48	6.57
205	35.45	75.87	2.10	75.90	1.59
180	37.00	77.75	-5.42	77.94	-3.99
155	39.59	78.41	-13.52	79.57	-9.78
130	44.21	74.72	-20.06	77.37	-15.03
105	51.51	64.76	-22.82	68.66	-19.41
80	60.64	51.34	-21.80	55.78	-23.01
55	72.04	32.97	-17.16	37.17	-27.50
30	82.34	16.94	-11.63	20.55	-34.47
15	88.32	8.03	-8.14	11.43	-45.39

[0070] [Table 3]

Working Example 2 <PV32 + PV19 (1 : 1) = total 2 wt.%>

Duty	L*	a*	b*	C*	h
255	37.32	78.13	-7.33	78.47	-5.36

130	38.79	78.69	-10.93	79.45	-7.91
205	40.48	79.77	-15.34	81.23	-10.89
180	42.57	78.10	-21.00	80.87	-15.05
155	46.61	74.85	-24.33	78.70	-18.01
130	52.84	67.37	-26.32	72.33	-21.34
105	59.82	54.22	-25.33	59.84	-25.04
80	67.28	40.71	-21.57	46.07	-27.92
55	75.83	27.48	-16.36	31.98	-30.77
30	83.86	15.22	-11.40	19.02	-36.83
15	88.63	7.85	-8.33	11.45	-46.70

[0071] [Table 4]

Working Example 3 <PV32 + PV19 (2 : 1) = total 4 wt.%>

Duty	L*	a*	b*	C*	h
255	32.35	73.15	22.28	76.47	16.94
130	33.10	74.34	16.23	76.09	12.32
205	34.12	75.96	10.28	76.65	7.71
180	35.73	77.67	1.66	77.69	1.22
155	38.37	78.19	-7.85	78.58	-5.73
130	43.23	74.37	-15.62	75.99	-11.86
105	50.60	64.84	-19.45	67.70	-16.70
80	60.04	51.11	-19.50	54.70	-20.88
55	71.76	33.12	-15.75	36.67	-25.43
30	82.71	17.06	-10.60	20.09	-31.85
15	88.91	8.13	-7.32	10.94	-42.00

[0072] [Table 5]

Working Example 4 <PV32 + PV19 (1 : 2) = total 4 wt.%>

Duty	L*	a*	b*	C*	h
255	35.41	76.55	13.08	77.66	9.70
130	36.32	77.49	7.49	77.85	5.52
205	37.69	78.70	1.01	78.71	0.74
180	39.79	79.75	-6.14	79.99	-4.40
155	43.39	78.05	-13.23	79.16	-9.62
130	49.02	71.37	-18.05	73.61	-14.19
105	56.79	59.90	-19.54	63.00	-18.07
80	66.09	44.78	-17.77	48.18	-21.64
55	76.47	28.31	-13.82	31.50	-26.02
30	85.02	14.68	-9.54	17.51	-33.02
15	90.05	7.03	-6.74	9.74	-43.79

[0073] [Table 6]

Comparative Example 1 <PR202: 4 wt.%>

Duty	L*	a*	b*	C*	h
255	36.25	78.56	5.95	78.78	4.33
230	36.95	79.32	1.98	79.34	1.43
205	38.19	80.18	-4.10	80.28	-2.93
180	40.19	80.82	-11.67	81.66	-8.22
155	43.04	78.31	-16.61	81.46	-13.21
130	47.18	74.34	-24.43	78.25	-18.19
105	52.72	65.11	-26.90	70.45	-22.45
80	59.90	52.12	-26.08	58.28	-26.58

55	69.57	35.63	-21.90	41.82	-31.58
30	80.27	19.00	-15.24	24.36	-38.73
15	87.30	9.41	-9.63	13.46	-45.66

[0074] [Table 7]

Comparative Example 2 <PV19: 4 wt.%>

Duty	L*	a*	b*	C*	h
255	44.15	79.38	26.25	83.6	18.3
230	44.78	79.83	22.6	83.0	15.8
205	45.84	80.51	16.54	82.2	11.6
180	47.23	80.88	8.75	81.4	6.2
155	49.28	81.07	0.71	81.1	0.5
130	52.35	78.7	-7.1	79.0	-5.2
105	56.72	72.49	-12.48	73.6	-9.8
80	62.55	62.04	-14.79	63.8	-13.4
55	71.1	45.32	-13.92	47.4	-17.1
30	81.07	25.64	-10.81	27.8	-22.9
15	87.56	12.94	-7.36	14.9	-29.6

[0075] [Table 8]

Comparative Example 3 <PV32: 4 wt.%>

Duty	L*	a*	b*	C*	h
255	30.09	69.36	31.76	76.3	24.6
230	30.67	70.28	28.43	75.8	22.0
205	31.6	71.9	22.37	75.3	17.3
180	32.87	74.09	13.96	75.4	10.7

155	34.68	76.37	3.61	76.5	2.7
130	37.83	76.95	-7.57	77.3	-5.6
105	43.81	71.43	-15.74	73.1	-12.4
80	52.33	59.99	-19.09	63.0	-17.7
55	63.64	43.14	-17.33	46.5	-21.9
30	76.97	23.85	-12.02	26.7	-26.7
15	85.74	11.9	-7.75	14.2	-33.1

[0076] FIG. 1 shows a graph in which the a* values of tables 2 to 8 are plotted against the abscissa and b* values are plotted against the ordinate.

FIG. 2 shows a graph in which the a* values of tables 2 to 8 are plotted against the abscissa and L* values are plotted against the ordinate. Of the graph shown in FIG. 2, the section with the a* value of 0 to 40 are shown in greater detail in FIG. 3 and the section with the a* values of 60 to 85 is shown in greater detail in FIG. 4.

[0077] FIG. 1 suggests that the ink compositions of Working Examples 1 to 4 and Comparative Examples 1 to 3 have almost identical color reproducibility. On the other hand, considering that the content of pigment solids in the ink composition of Working Example 2 is lower than that of other ink compositions, the ink composition in accordance with the invention clearly has excellent color reproducibility.

[0078] FIG. 3 demonstrates that the ink composition of Comparative Example 2 has an L* value in a low-a* region higher than that of the ink compositions of Working Examples 1 to 4 and excels in granularity. However, as shown in FIG. 4, it has poor coloring ability of a dark section in the high-a* region. On the other hand, the ink compositions of Comparative Example 1 and Comparative Example 3, conversely to the ink composition of Comparative Example 2, have coloring ability of a dark section in the high-a* region on par with that of the ink compositions of Working Examples 1 to

4, but the L* value thereof in a low-a* region is low and granularity is poor. The ink compositions of Working Examples 1 to 4 have excellent balance of granularity and coloring ability of a dark section. Thus, it is clear that they have excellent color reproducibility in a high-chroma and low-lightness red region and also excel in granularity.

[0079] (Measurement of L*, a*, b* values of diluted aqueous solution of magenta ink)

Magenta inks of working examples and comparative examples were prepared so that the pigment concentration of any one type of mixtures of PV32 and PV19 (mixing ratios 1:1, 2:1, 1:20), PV32, PV19 and PR202 was 4 wt.%, and then the inks were diluted with water to obtain an a* value of 80. The aqueous solution comprising a 1:1 mixture of PV32 and PV19 had to be diluted at a ratio of about 1000, the aqueous solution comprising a 2:1 mixture of PV32 and PV19 had to be diluted at a ratio of about 1160, an aqueous solution comprising a 1:2 mixture of PV32 and PV19 had to be diluted at a ratio of about 910, the aqueous solution comprising PR202 had to be diluted at a ratio of about 660, the aqueous solution comprising PV19 had to be diluted at a ratio of about 500, and the aqueous solution comprising PV32 had to be diluted at a ratio of about 1500. Table 9 shows the measurement results for the L* value and b* value in each diluted aqueous solution.

Measurements of L* value, a* value, and b* value of each aqueous solution were conducted by using U3300 manufactured by Hitachi Ltd. More specifically, transmittance measurements were carried out at a scan speed of 600 nm/min, a measurement wavelength range of 380-800 nm, and a slit width of 2.0 nm and calculations were conducted for a view angle of 2° and a D65 light source.

[0080] The results are shown in Table 9 below. The type, mixing ratio and concentration of the pigment are shown in the column at the left side of Table 9.

From top to bottom, the data correspond to ink compositions of a Working Example 1, Working Example 3, Working Example 4, Comparative Example 1, Comparative Example 2, and Comparative Example 3. Because the coloring component contained in the ink compositions is only the pigment, it is obvious to a person skilled in the art, that if the ink composition of Working Example 2 is diluted at a ratio of about 500, the L* value and b* value will be similar to the (PV 19 + PV32 = 1:1)_4%.

[0081] [Table 9]

	a*80		
	L*	b*	Dilution ratio
(PV19 + PV32 = 1:1)_4%	51.07	-34.09	About 1000
(PV19 : PV32 = 1:2)_4%	51.87	-35.26	About 1160
(PV19 : PV32 = 2:1)_4%	54.64	-30.26	About 910
PR202_4%	50.92	-28.63	About 660
PV19_4%	61.04	-16.72	About 500
PV32_4%	49.51	-38.60	About 1500

[0082] For the ink compositions of Working Examples 1 to 4, it can be confirmed that when the a* value was 80, the b* value was -38 or more to -29 or less and the L* value was 60 or less.

[0083] Then, aqueous solutions comprising 2% of pigment of one type were prepared for magenta ink compositions of each working example and comparative example and diluted at a ratio of 10,000 to obtain aqueous solutions with a pigment concentration of 2×10^{-3} g/L. L*, a*, and b* values were then measured by the above-described methods. The results are shown in Table 10.

[0084] [Table 10]

Dilution ratio	10,000

	L*	a*	b*
(PV19 + PV32)_2%	95.19	7.45	-3.85
(PV19 : PV32 = 1:2)_2%	94.60	9.07	-5.23
(PV19 : PV32 = 2:1)_2%	96.33	6.76	-3.38
PR202_2%	97.15	3.41	-2.81
PV19_2%	97.50	5.28	-1.86
PV32_2%	93.98	9.27	-6.16

[0085] In the ink compositions of Working Examples 1 to 4, the a* value was confirmed to be 5 or more in n aqueous solution with a pigment concentration of 2 x 10^{-3} g/L.

[0086] The above-described results confirmed that the magenta ink composition in which when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is -38 or more to -29 or less (preferably, the L* value in accordance with the CIE standard that is calculated under the same conditions is 60 or less, and the magenta ink in which the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 5 or more in a diluted aqueous solution with a pigment concentration of 2 x 10^{-3} g/L have excellent color reproducibility in a high-chroma and low-lightness region, are rich in luster, and hardly cause any clogging of ink-jet recording heads.

[Industrial Applicability]

[0087] The present invention is industrially applicable as a magenta ink with improved glossiness that has excellent color reproducibility in regions of low brightness and high color saturation and is highly resistant to clogging of the inkjet recording head, as an ink cartridge, and as a recording method, recording system and

recorded matter using the magenta ink composition.

[Brief Description of the Drawings]

[0088] FIG. 1 is a graph illustrating the relationship between b* values and a* values of magenta inks with pigments of different types.

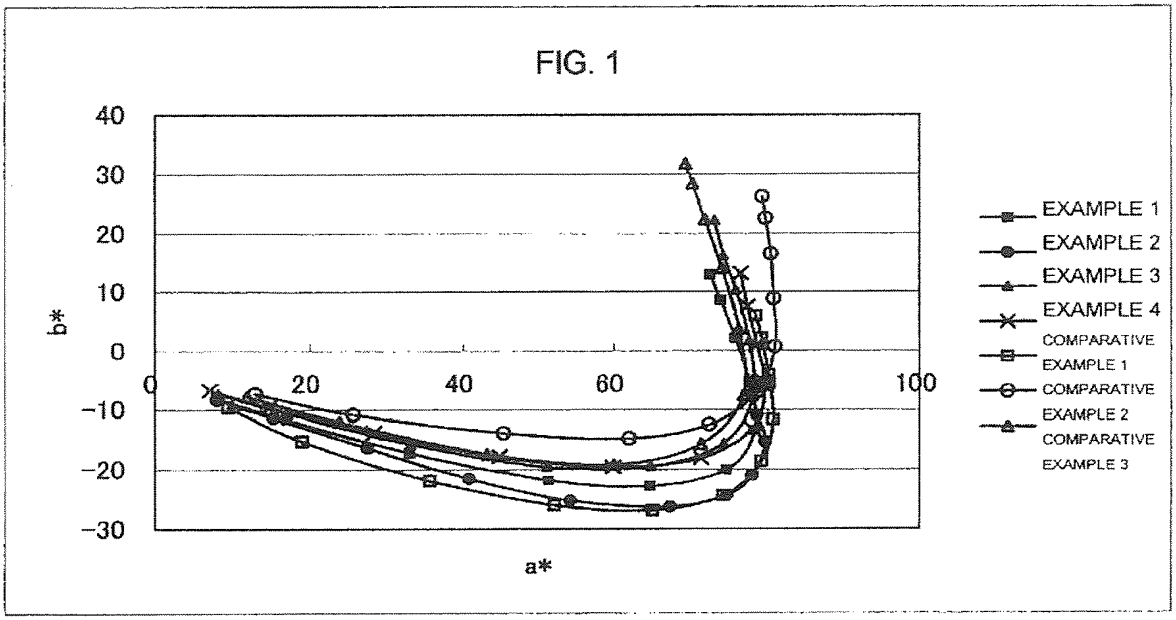
FIG. 2 is a graph illustrating the relationship between L* values and a* values of magenta inks with pigments of different types.

FIG. 3 is an enlarged via of part of the graph shown in FIG. 2 (low-chroma region).

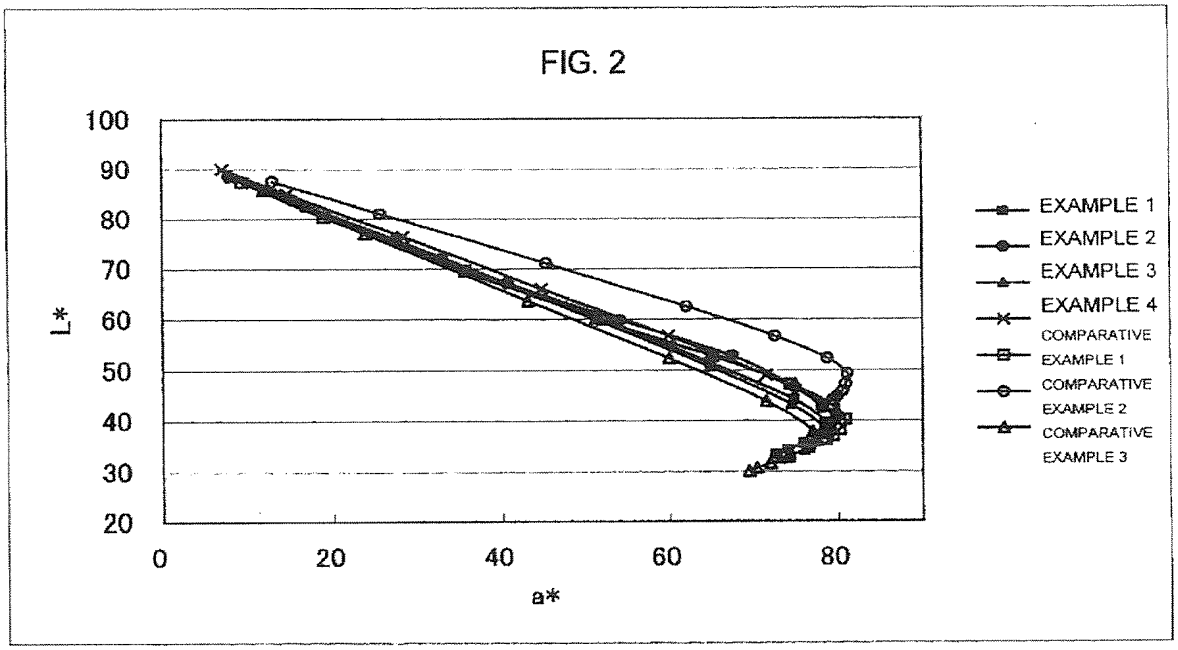
FIG. 4 is an enlarged via of part of the graph shown in FIG. 2 (high-chroma region).

[Name of Document] Drawings

[FIG. 1]

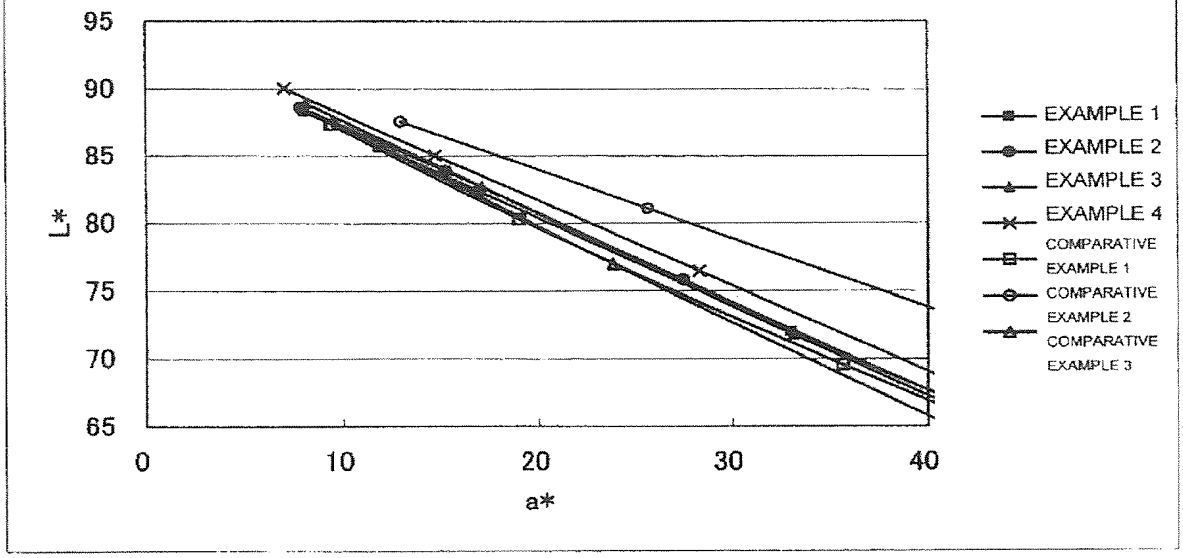


[FIG. 2]



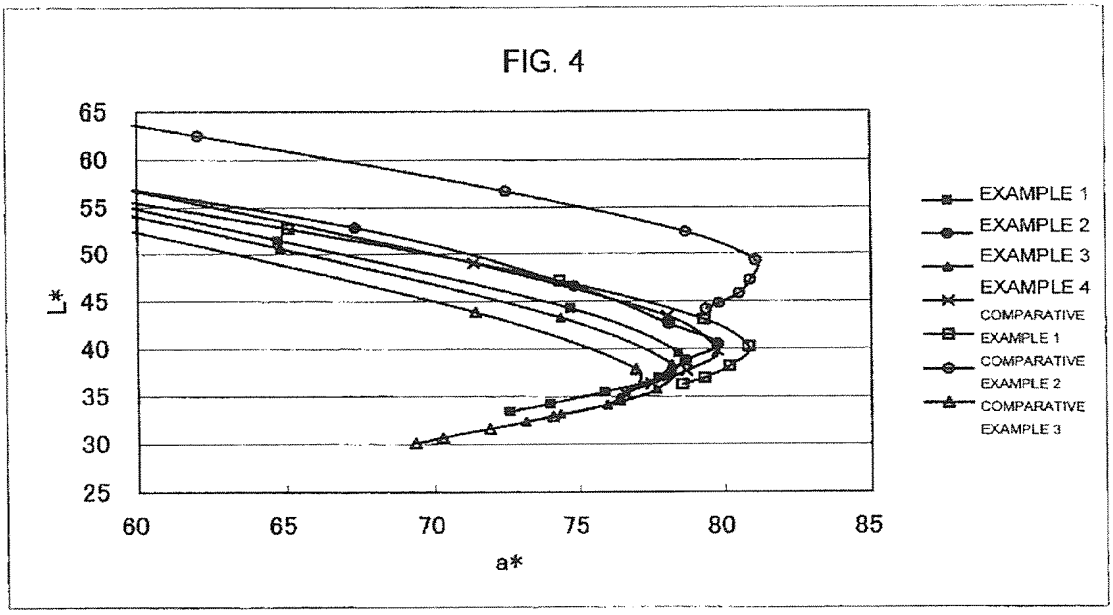
[FIG. 3]

FIG. 3



[FIG. 4]

FIG. 4



[Name of Document] Abstract

[Abstract]

[Problem] The object of the present invention is to provide a magenta ink that excels in color reproducibility in a high-chroma and low-lightness region, suppresses clogging of ink-jet recording heads, and has increased luster.

[Solution] The present invention provides a magenta ink composition, in which when the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b* value is –38 or more to -29 or less, and the magenta ink composition in which the a* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 5 or more in a diluted aqueous solution with a pigment concentration of 2×10^{-3} g/L.

[Selected Drawing] None